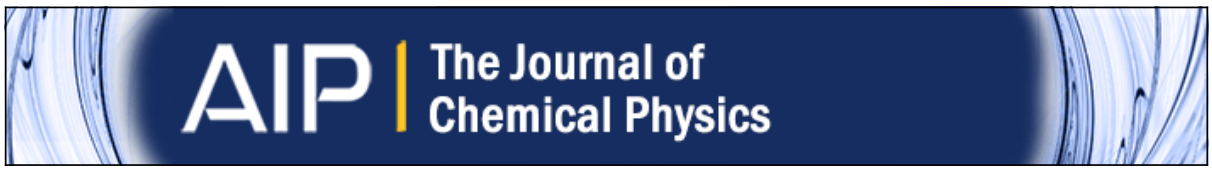

On the use of F and G sum rules as error indicators of experimental vibrational intensity data: The CH x D3−x Br molecules

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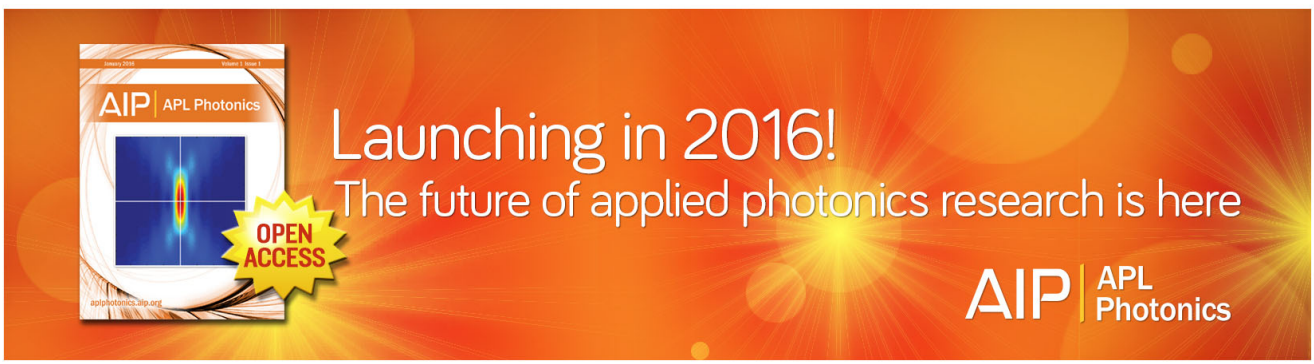

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On the use of *F* and *G* sum rules as error indicators of experimental vibrational intensity data: The $CH_xD_{3-x}Br$ molecules

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Considering only the *G* sum rule results for the methyl bromides, one would not ascribe a large systematic error to the CD_3Br data and negligible systematic errors to the data for the other bromides.[1,2] More likely one would conclude that smaller systematic errors contribute to the intensity data for all these molecules. The *F* sum rule results (Table I of Ref. 1 and Table II of Ref. 2) dramatically point out the isolated position of the CD_3Br data relative to those of the other methyl bromides. Errors due to uncertainties in the harmonic frequencies and fundamental band separations can make the *F* sum rule results more approximate than those of the *G* sum rule as Professor Smit has pointed out.[1] If such errors are large, the conclusions based on the *F* sum rule results should be made subordinate to those of the *G* sum rule.

The harmonic oscillator–linear dipole approximation is normally not expected to cause serious errors in analyses involving the *F* and *G* intensity sum rules. As Crawford[3] has written, "the effects of anharmonicities on the intensities of fundamentals are of the *second* order, although the effects on frequencies are *first* order; it may be, therefore, that these intensity rules will be followed *more* closely than is the (frequency) product rule." Certainly, our experience in applying these rules to the methane family (CH_xD_{4-x}, $x=0,1,2,\ldots,4$) indicates that errors due to this approximation are much smaller[4] than the reported experimental errors.[5] As these errors for the methanes are of the same percentage size as those for the methyl bromides,[6] how can the apparent inconsistencies in the *F* and *G* sum rule data for the latter molecules be explained?

Yao and Overend[7] express the transition moment matrix element for the fundamental band as

$$\langle v_s, v_{s'} \,|\, P' \,|\, v_{s+1}, v_{s'} \rangle = P_s[(v_s+1)/2]^{1/2}\left[1 + C'(v_s+1) + \sum_{s' \neq s} D_{s'}(v_{s'}+\tfrac{1}{2})\right],$$

where the terms involving C' and $D_{s'}$ are *second* order perturbation corrections to the harmonic oscillator–linear dipole contribution. The definitions for the symbols in this equation can be found in Ref. 7. C' and $D_{s'}$ are not only functions of high order constants in the potential energy and dipole moment functions but also depend on terms containing $(4\omega_s^2 - \omega_{s'}^2)$ in their denominators, with ω_s and $\omega_{s'}$ indicating different harmonic fundamental frequencies. As such terms are summed over all $s' \neq s$ the terms included in C' and $D_{s'}$ may become large if a fundamental frequency is approximately equal to that of an overtone. In the absence of resonance effects these terms are expected to be small. This has been confirmed by the analysis of fundamental and overtone intensities for diatomic molecules.[8] For the methane series these terms also appear to be too small to detect using the *G* sum rule because of experimental error.

On the other hand intensity borrowing through quantum mechanical resonance is known for CH_3Br and CD_3Br where $2\nu_5 \approx \nu_1^5$. Unfortunately C' and $D_{s'}$ can not be evaluated due to the lack of relevant data. However, this kind of breakdown in the harmonic oscillator–linear dipole approximation might explain, to some extent, why the *F* and *G* sum rules are obeyed by the intensity data of the methanes but not by the methyl bromide data.

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Comment on "Environmental effects on radiative rate constants with applications to linear polyenes"

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In a recent paper,[1] Andrews and Hudson developed a theory of solvent effects on radiative rate constants using first-order perturbation theory with vibronic coupling along with solvent-dependent energy denominators. The final expressions of this theory contained no provisions for solvent effects on the wave functions. This approach was partially justified by their claim that they had shown that the direct solvent contribution to the radiative rate constant of a nominally forbidden state must vanish when the solute and solvent are nonpolar and when certain symmetry conditions hold. In particular, they were concerned with the dispersion force and with inversion symmetry. In the following, it will be shown that if all the decay channels are properly taken into account, the direct solvent contribution to the radiative rate constant will be nonzero.

The simplest way to proceed is to take as a counterexample a model where the solvent lattice is considered to be a set of harmonic oscillators. The conditions of inversion symmetry and the dispersion force can then be assumed. The initial state of the system should be represented by a Boltzmann distribution in the solvent oscillators. For the sake of argument it is only necessary to consider the vibrationless state for the solvent in the initial composite solute–solvent state.

$$\psi^{(0)}_{\text{initial}} = U_a \xi_0(q', Q')\eta_{00}(Q'')\,|\,0_1, 0_2, \ldots, 0_N\rangle$$
$$= \phi_a(q, Q)\chi_{a0}(Q)\xi_0(q', Q')\eta_{00}(Q'')\,|\,0_1, 0_2, \ldots, 0_N\rangle\,, \quad (1)$$

where $U_a = \phi_a(q, Q)\chi_{a0}(Q)$ is the initial solute state written in the Born–Oppenheimer representation and $\xi_0(q', Q')\eta_{00}(Q'')|\,0_1, 0_2, \ldots, 0_N\rangle$ is the solvent state with $|\,0_1, 0_2, \ldots, 0_N\rangle = |\,0_1\rangle\,|\,0_2\rangle \cdots |\,0_N\rangle$ being the vibrationless state of the solvent lattice written out explicitly in the occupation number representation to emphasize the role of lattice vibrations. In the occupation number representation used here, the subscripts are meant to refer to the specific lattice sites and not to the normal modes. The set of internal vibrations of the solvent molecules will be called Q''; and the set of all solvent vibrations, both Q'' and the lattice vibrations, will be labeled Q'. The function $\eta_{00}(Q'')$ is the vibrational wave function for the internal vibrations of the solvent molecules when the solvent electronic state is ξ_0. As pointed out previously,[1] the dispersion interaction causes only certain types of intermediate states to mix with the initial composite state in first order. Specifically,

$$\psi_{\text{initial}} = \psi^{(0)}_{\text{initial}} + \sum_i R_i^{-3} \sum_{n,m} \frac{\langle U_n|\,\mu_u\,|\,U_a\rangle \Theta^i_{an,0m} \langle V_m|\,\mu_i\,|\,V_0\rangle}{(E^u_a - E^u_n) + (E^v_0 - E^v_m)} U_n V_m\,. \quad (2)$$

This is the same equation as Eq. (8) in Ref. 1 except here the energy denominators are zero-order in the solute–solvent interaction and $V_0 = \xi_0(q', Q')\eta_{00}(Q'')|\,0_1, 0_2, \ldots, 0_N\rangle$ and $V_m = \xi_0(q', Q')\eta_{00}(Q'')|\,0_1, 0_2, \ldots, 1_m, \ldots, 0_N\rangle$. Notice that the summation over n includes all intermediate *vibronic* states of the solute. Whereas that over m, while in principle spanning the entire set of solvent vibronic-lattice levels is, in practice, limited to the lattice manifold associated with the initial solvent vibronic state. By the nature of the interaction both solute and solvent components must undergo transitions.[2] In the case considered here, the intermediate composite state has a solute component that has a nonzero transition moment to the ground state of the solute[3] and has a solvent component that has the mth harmonic oscillator in the first excited state. This intermediate state can make a significant contribution to the radiative rate constant if the final state is a composite state with the solute in the ground state and the solvent in the first excited state of the mth harmonic oscillator. For instance, one of the possible final channels that must be taken into account for the total radiative rate constant is the state $U_0 V_k = \psi^{(0)}_{k,\text{final}}$, where U_0 is any vibronic state in the manifold associated with the electronic ground state of the solute.

Ignoring solvent effects on this final wave function, as was done in Ref. 1, the direct solvent contribution to the decay amplitude from this channel is

$$\langle \psi^{(0)}_{k,\text{final}}|\,\mu_u\,|\,\psi_{\text{initial}}\rangle = \sum_i R_i^{-3} \sum_n \frac{\langle U_n|\,\mu_u\,|\,U_a\rangle \Theta^i_{an,0k} \langle V_k|\,\mu_i\,|\,V_0\rangle}{(E^u_a - E^u_n) + (E^v_0 - E^v_k)} \times \langle U_0|\,\mu_u\,|\,U_n\rangle \langle V_k\,|\,V_k\rangle\,. \quad (3)$$

These final states with one or more quanta of lattice vibrations present are quite common in solid state spectroscopy.[4,5]

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